

事務連絡

平成27年11月19日

各都道府県衛生主管部（局）薬務主管課 御中

厚生労働省医薬・生活衛生局審査管理課

生理処理用品材料規格の英訳について

医薬部外品のうち、生理処理用品の材料規格については、「生理処理用品材料規格について」（平成27年3月25日付け薬食審査発0325第24号厚生労働省医薬食品局審査管理課長通知）により示してきたところですが、別添のとおり、当該規格の英訳を作成したのでお知らせいたします。



Provisional Translation  
from Japanese Original

Mar 25, 2015

Notification PFSB/ELD No.0325-24

# **The Japanese Specifications of Sanitary Napkin**

## **Materials**

## <1. General Notices>

1. This standard is entitled "The Japanese Specifications of Sanitary Napkin Materials" and may be abbreviated as "JSNM". The napkin materials generally used are listed in Part 1 and the colorants are listed in Part 2.
2. The specifications and test methods shall be in accordance with the General Notices and the General Tests, Processes and Apparatus of the Japanese Pharmacopoeia when they are not specified in the General Notices, General Tests, Processes and Apparatus, and Monographs of the JSNM. The Japanese Pharmacopoeia (hereinafter referred to as JP) is specified in the Law for Ensuring the Quality, Efficacy, and Safety of Drugs and Medical Devices (Law No. 145, 1960) and the Japanese Industrial Standards (herein after referred to as JIS) are specified in the Industrial Standardization Act (Law No. 185, 1949).
3. The commonly used name and English name are indicated after the title of the napkin material in each monograph, as appropriate.
4. Napkin materials are to be tested according to the provisions given in the pertinent monographs, General Notices, and General Tests for their conformity to JSNM.
5. The molecular formula is additionally indicated in parentheses after the chemical name. Atomic masses adopted in JSNM conform to the table of "Standard Atomic Weights 2004". Molecular masses are indicated to two decimal places rounded from three decimals.
6. The following abbreviations are used for the principal units. The SI system is used for other units.

meter	m	centimeter	cm	millimeter	mm
micrometer	$\mu\text{m}$	nanometer	nm	per centimeter	$\text{cm}^{-1}$
ton	t	kilogram	kg	gram	g
milligram	mg	microgram	$\mu\text{g}$	liter	L
milliliter	mL	microliter	$\mu\text{L}$	square centimeter	$\text{cm}^2$
kilopascal	kPa	mole per liter	mol/L		
7. The signs "%," "w/v%," "vol%," and "v/w%" are used for mass per cent, mass per volume per cent, volume per cent, and volume per mass per cent, respectively. "ppm" usually indicates mass parts per million.
8. The temperature is expressed in Celsius degree as Arabic numerals followed by °C.

9. Standard temperature, ordinary temperature, room temperature, and lukewarm are defined as 20°C, 15-25°C, 1-30°C, and 30-40°C, respectively. A cold place, unless otherwise specified, shall be a place having a temperature not exceeding 15°C. The temperature of cold water, lukewarm water, warm water, and hot water are defined as not exceeding 10°C, 30-40°C, 60-70°C, and about 100°C, respectively. The term "heated solvent" or "hot solvent" means a solvent heated almost to the boiling point of the solvent, and the term "warmed solvent" or "warm solvent" usually means a solvent heated to a temperature between 60°C and 70°C. The term "heat on or in a water bath" indicates, unless otherwise specified, heating with a boiling water bath or a steam bath at about 100°C.

10. To measure the number of drops, a dropping device which delivers 20 drops of Purified Water (JP) weighing 0.90-1.10 g at 20°C shall be used.

11. The term "in vacuum" indicates, unless otherwise specified, a pressure not exceeding 2.0 kPa.

12. The acidity or alkalinity of a solution, unless otherwise specified, is determined by blue or red litmus papers. To indicate these properties more precisely, pH values are used. Such expressions as "slightly acidic", "weakly/mildly acidic", "strongly acidic", "slightly alkaline", "weakly/mildly alkaline" and "strongly alkaline" indicate approximate degrees of acidity or alkalinity, which respectively correspond to the following pH ranges:

	pH range (approx.)		pH range (approx.)
Slightly acidic	5-6.5	Slightly alkaline	7.5-9
Weakly acidic	3-5	Weakly alkaline	9-11
Strongly acidic	Not more than 3	Strongly alkaline	Not less than 11

13. Unless otherwise specified, the matching fluids for color, reagents, test solutions, standard solutions, standard solutions for volumetric analysis, reference standards, measuring instruments and appliances to be used in the General Notices, General Tests and monographs of JSNM shall be those specified in the General Tests. Unless otherwise specified, the water to be used in the tests shall be Purified Water (JP).

14. As for wording "solution", where the name of the solvent is not stated, the term "solution" indicates a solution in water.

15. For solution an expression such as "(1 in 3)", "(1 in 10)", or "(1 in 100)" means that 1 g of a solid is dissolved in, or 1 mL of a liquid is diluted with the solvent to make the total volume of 3 mL, 10 mL or 100 mL, respectively. For the liquid mixture an expression such as "(10:1)" or "(5:3:1)" means that the respective numbers of parts, by volume, of the designated liquids are to be mixed.

16. The term "weigh accurately" means to weigh down to the degree of 0.1 mg, 0.01 mg or 0.001 mg by

taking into account the purpose of the test and using a relevant weighing device. The term “weigh exactly” means to weigh to the given decimal places.

17. A value of “n” figures in a test of a napkin material shall be obtained by rounding off a value of “n+1” figures.
18. Unless otherwise specified, all tests of the napkin materials shall be performed at the ordinary temperature and observations of the results shall follow immediately after the operations. However, the judgment for a test which is affected by temperature should be based on the conditions at the standard temperature.
19. The term “description” in the monograph states the color, shape, and odor of the napkin material as a reference. In the section under the heading Description, the term “white” is used to indicate white or practically white. Unless otherwise specified, the test of color is carried out by placing 1 g of a solid material on a sheet of white paper or in a watch glass placed on white paper. A liquid material is put into a colorless test tube of 15-mm internal diameter and is observed in front of a white background through a layer of 30 mm. The term “odorless” is used to indicate odorless or practically odorless. Unless otherwise specified, the test of odor shall be carried out by placing about 1 g of a solid material or about 1 mL of a liquid material in a 100-mL beaker.
20. “Identification” is the test necessary to identify the specific component(s) of a napkin material based upon its specific property.
21. “Characteristic value” is to test the characteristics of a napkin material, generally is to specify its physicality, state, and the range of composition.
22. “Purity” is the test to detect impurities/contaminants in napkin materials, and it, as well as other requirements in each monograph, specifies the purity of the material usually by limiting the kind/nature and quantity of the impurities/contaminants. The impurities/contaminants subject to the purity test are those supposed to generate/contaminate during the manufacturing process or storage, including hazardous agents such as heavy metals, arsenic, etc. In the fluorescence test of a material, the term “marked fluorescence” indicates that the fluorescence of the material is more intense than Fluorescence Reference Standard and has a certain extensity partially.
23. In the test of a napkin material, the term “dissolve” or “miscible” indicates that it dissolves in, or mixes in arbitrary proportion with the solvent to form a clear solution or mixture. Insoluble materials other than the material including fibers should not be detected or practically invisible, if any.

24. In the test of a napkin material, the terms "immerse", "macerate" and "perform cold extraction", mean that the material is to be soaked in water for at least 5 minutes. unless solvent specified,
25. The term "constant mass" in drying or ignition, means that the mass difference after an additional 1 hour of drying or ignition is not more than 0.10% of the preceding mass of the dried substance or ignited residue. However, when the difference does not exceed 0.5 mg in a chemical balance, 0.05 mg in a semi-microbalance, or 0.005 mg in a microbalance, the difference is regarded as negligible and constant mass has been attained.
26. In stating the sample quantity to be taken, the use of the word "about" indicates a quantity within 10% of the specified mass.
27. The test methods specified in JSNM may be selected on the basis of the characteristics of the napkin material.
28. Alternative test methods which are better than the test methods specified in JSNM in precision and accuracy can be substituted. However, where a difference is suspected in test results, the procedure given in the JSNM is followed for the final judgment.

## <2. General Tests, Processes and Apparatus>

1. **Acrylic Unreacted Monomer Test**
2. **Liquid Chromatography**
3. **Chloride Limit Test**
4. **Flame Coloration Test (for Metallic Salts)**
5. **Total Ash Test**
6. **Gas Chromatography**
7. **Loss on Drying Test**
8. **Ultraviolet-visible Spectrophotometry (Former name: Spectrophotometry)**
9. **Residue on Ignition Test**
10. **Saponification Value Determination**
11. **Atomic Absorption Spectrophotometry**
12. **Acid Value Determination**
13. **Heavy Metals Limit Test**
14. **Infrared Spectrophotometry**
15. **Qualitative Tests**
16. **Viscosity Determination**
17. **pH Determination**
18. **Determination of Specific Gravity and Density**
19. **Arsenic Limit Test**
20. **Melting Point Determination**
21. **Readily Carbonizable Substances Test**
22. **Standard Solutions, Matching Fluids for Color, Reference Standards, Reagents, Test Solutions, Measuring Instruments and Appliances**

## 1. Acrylic Unreacted Monomer Test

Acrylic Unreacted Monomer Test is a method to measure the unreacted monomer with double bonds mainly in an acrylic sample.

### Procedure

Unless otherwise specified, weigh accurately the amount of sample conforming to the monograph, in a 300-mL iodine flask. Add 100 mL of water and stir for 1 hour for dispersion. To the solution add exactly 5 mL of potassium bromate-potassium bromide TS with stirring, add quickly 20 mL of diluted hydrochloric acid (1 in 4), and stopper immediately and tightly. Place 10 mL of potassium iodide TS on the upper stopper of the iodine flask, and allow to stand in a dark place for 20 minutes while shaking occasionally. Take out the iodine flask from a dark place, pour potassium iodide TS placed on the upper stopper into the flask, immediately stopper tightly, and shake sufficiently. Use the solution as the sample solution and titrate with 0.1 mol/L sodium thiosulfate VS (indicator: 2 mL of starch TS) until the color of the sample solution changes from deep purple to colorless, and titrate by continuous shaking for 10 minutes until no color develops again. Separately, perform a blank determination, and calculate the content of unreacted monomer from the following equation.

$$\text{Content (\% of unreacted monomer)} = \frac{0.0047(a-b)}{c} \times 100(\%)$$

- a: Volume (mL) of 0.1 mol/L sodium thiosulfate VS consumed in a blank determination
- b: Volume (mL) of 0.1 mol/L sodium thiosulfate VS consumed of the sample
- c: Amount (g) of sample

## 2. Liquid Chromatography

Liquid Chromatography is a method to develop a mixture injected into a column prepared with a suitable stationary phase by passing a liquid as a mobile phase through the column, in order to separate the mixture into its components by making use of the difference of retention capacity against the stationary phase, and to determine the components. This method can be applied to a liquid or soluble sample, and is used for identification, purity test, and quantitative determination.

A mixture injected into the column is distributed between the mobile phase and the stationary phase with a characteristic ratio ( $k$ ) for each component.

$$k = \frac{\text{amount of compound in the stationary phase}}{\text{amount of compound in the mobile phase}}$$

The ratio  $k$  represents the mass distribution ratio (or the capacity factor)  $k'$  in liquid chromatography.

Since the relation given below exists among the ratio ( $k$ ), the time for which the mobile phase is passed through the column ( $t_0$ : time measured from the time of injection of a compound with  $k=0$  to the time of elution at the peak maximum), and the retention time ( $t_R$ : time measured from the time of injection of a compound to be determined to the time of elution at the peak maximum), the retention time for a compound on



a column has a characteristic value under fixed chromatographic conditions.

$$t_R = (1 + k) t_0$$

### **Apparatus**

Basically, the apparatus required for the liquid chromatographic procedure consists of a pumping system for the mobile phase, a sample injection port, a column, a detector and a recorder. A mobile phase component regulator, a thermostat for the column, a pumping system for reaction reagents and a chemical reaction chamber are also used, if necessary. The pumping system serves to deliver the mobile phase and the reagents into the column and connecting tube at a constant flow rate. The sample injection port is used to deliver a quantity of the sample to the apparatus with high reproducibility. The column is a tube with a smooth interior, made of inert metal, etc., in which a packing material for liquid chromatography is uniformly packed. A column with a stationary phase chemically bound on the inside wall instead of the column packed with the packing material may be used. The detector is used to detect a property of the samples which is different from that of the mobile phase, and may be an ultraviolet or visible spectrophotometer, fluorometric detector, differential refractometer, electrochemical detector, chemiluminescence detector, electric conductivity detector, mass spectrophotometer, etc. The output signal is usually proportional to the concentration of samples at amounts of less than a few  $\mu\text{g}$ . The recorder is used to record the output signals of the detector. As required, a data processor may be used as the recorder to record or output the chromatogram, retention times, or amounts of the components. The mobile phase component regulator is used to vary the ratio of the mobile phase components in a stepwise or gradient fashion.

### **Procedure**

Fix the detector, column and mobile phase to the apparatus, and adjust the flow rate and the column temperature to the values described in the operating conditions specified in the individual monograph. Inject a volume of the sample solution or the standard solution specified in the individual monograph with the sample injector into the column through the sample injection port. The separated components are detected by the detector, and recorded by the recorder as a chromatogram. If the components to be analyzed have no readily detectable physical properties such as absorbance or fluorescence, the detection is achieved by changing the components to suitable derivatives. Usually, the derivatization is performed as a pre- or post-column labeling.

### **Identification and purity test**

Identification of a component of a sample is performed by confirming agreement of the retention time of the sample with that of an authentic specimen, or by confirming that the peak shape of the sample is unchanged after mixing the sample with an authentic specimen.

In general, the purity of the sample is determined by comparing the sample solution with a standard solution, which is prepared by diluting the sample solution to a concentration corresponding to the specified limit amount of the impurity, or by the peak area percentage method. Unless otherwise specified, if a sample is separated into isomers in the chromatogram, the isomer ratio is calculated by using the peak area percentage method.

The peak area percentage method is a method to calculate the proportion of the components from the ratio of the peak area of each component to the sum of the peak areas of every peak recorded in the chromatogram. In order to obtain accurate results in evaluating the proportion of the components, it is necessary to correct the

area of each component based on the relative sensitivity to the principal component.

### 3. Chloride Limit Test

Chloride Limit Test is a limit test for chloride contained in a sample. In each monograph, the permissible limit for chloride (as Cl) is described in terms of percentage (%) in parentheses.

#### Procedure

Unless otherwise specified, transfer the quantity of the sample, directed in the monograph, to a Nessler tube, dissolve it in sufficient water, and add water to make 40 mL. Add 6 mL of dilute nitric acid and water to make 50 mL, and use this solution as the sample solution. Transfer the volume of 0.01 mol/L hydrochloric acid VS, directed in the monograph, to another Nessler tube, add 6 mL of dilute nitric acid and water to make 50 mL, and use this solution as the control solution. When the sample solution is not clear, filter both solutions according to the same procedure.

Add 1 mL of silver nitrate TS to the sample solution and to the control solution, mix well, and allow to stand for 5 minutes protecting from direct sunlight. Compare the opalescence developed in both solutions against a black background by viewing downward or transversely.

The turbidity produced in the sample solution is not thicker than that of the control solution.

### 4. Flame Coloration Test (for Metallic Salts)

Flame Coloration Test is a method to detect an element, by means of the property that the element changes the colorless flame of a Bunsen burner to its characteristic color.

#### Procedure

The platinum wire used for this test is about 0.8 mm in diameter, and the end part of it is straight. In the case of a solid sample, make the sample into a gruel by adding a small quantity of hydrochloric acid, apply a little of the gruel to the 5-mm end of the platinum wire, and test by putting the end part in a colorless flame, keeping the platinum wire horizontal. In the case of a liquid sample, immerse the end of the platinum wire into the sample to about 5 mm in length, remove from the sample gently, and perform the test in the same manner as for the solid sample.

### 5. Total Ash Test

Total Ash Test is a method to measure the total amount of ash in a sample.

#### Procedure

Ignite previously a crucible of platinum, quartz or porcelain between 500°C and 550°C for 1 hour. Cool, and

weigh accurately the crucible. Unless otherwise specified, weigh accurately 2 to 4 g of the test sample for analysis in this crucible, take off the lid or keep it open a little if necessary, heat the crucible at a low temperature at first, then gradually heat to a temperature between 500°C and 550°C, ignite to incinerate the residue for more than 4 hours until no carbonized substance remains in the ash, cool and weigh accurately the ash. Incinerate repeatedly to constant mass, cool, weigh accurately, and determine the amount (%) of total ash. If a carbonized substance remains and a constant mass cannot be obtained in the above-mentioned method, extract the charred mass with hot water, collect the insoluble residue on filter paper for assay, and incinerate the residue and filter paper until no carbonized substance remains in the ash. Then add the filtrate, evaporate it to dryness, and incinerate. Cool, weigh accurately, and determine the mass (%) of the total ash. If a carbon-free ash cannot be obtained even in this way, moisten the ash with a small amount of ethanol (95), break up the ash with a glass rod, wash the rod with a small amount of ethanol (95), evaporate carefully, and determine the mass of the total ash as described above. A desiccator (silica gel) is used for cooling.

## 6. Gas Chromatography

Gas Chromatography is a method to develop a mixture injected into a column prepared with a suitable stationary phase by passing a gas (carrier gas) as a mobile phase through the column, in order to separate the mixture into its components by making use of the difference of retention capacity against the stationary phase, and to determine the components. This method can be applied to a gaseous or vaporizable sample, and is used for identification, and purity test.

A mixture injected into the column is distributed between the mobile phase and the stationary phase with a characteristic ratio ( $k$ ) for each component.

$$k = \frac{\text{amount of compound in the stationary phase}}{\text{amount of compound in the mobile phase}}$$

Since the relation given below exists among the ratio ( $k$ ), the time for which the mobile phase is passed through the column ( $t_0$ : time measured from the time of injection of a compound with  $k=0$  to the time of elution at the peak maximum), and the retention time ( $t_R$ : time measured from the time of injection of a compound to be determined to the time of elution at the peak maximum), the retention time for a compound on a column has a characteristic value under fixed chromatographic conditions.

$$t_R = (1+k) t_0$$

### Apparatus

Basically, the apparatus required for the gas chromatographic procedure consists of a carrier gas-introducing port and flow regulator, a sample injection port, a column, a column oven, a detector and a recorder. Gas introducing port and flow regulator for a combustion gas, a burning supporting gas and an accessory gas and sample injection port for headspace are also used, if necessary.

The carrier gas-introducing port and flow regulator serves to deliver the carrier gas into the column at a constant flow rate, and usually consist of a pressure regulation valve, a flow rate regulation valve and a

pressure gauge. The sample injection port is used to deliver a quantity of the sample to the flow line of carrier gas with high reproducibility. There are sample injection ports for packed column and for capillary column. There are both divided injection mode and non-divided injection mode to sample injection port for capillary column. The columns are usually classified as packed column or capillary column. The packed column is a tube made of inert metal, glass or synthetic resin, in which a packing material for gas chromatography is uniformly packed. The packed column with not more than 1mm in inside diameter is also called a packed capillary column (micro packed column). A capillary column is a tube made of inert metal, glass, quartz or synthetic resin, whose inside wall is bound chemically with stationary phase for gas chromatography. The column oven has the setting capacity for a column with required length and the temperature regulation system for keeping the constant column temperature. The detector is used to detect a component separated on the column, and may be an alkaline thermal ionization detector, a flame photometry detector, mass spectrophotometer, hydrogen flame-ionization detector, an electron capture detector, a thermal conductivity detector, etc. The recorder is used to record the output signals of the detector.

#### **Procedure**

Unless otherwise specified, proceed by the following method. Fix the detector, column and carrier gas to the apparatus, and adjust the flow rate and the column temperature to the values described in the operating conditions specified in the individual monograph. Inject a volume of the sample solution or the standard solution specified in the individual monograph with the sample injector into the system. The separated components are detected by the detector, and recorded by the recorder as a chromatogram.

#### **Identification and purity test**

Identification of a component of a sample is performed by confirming agreement of the retention time of the sample with that of an authentic specimen, or by confirming that the peak shape of the sample is unchanged after mixing the sample with an authentic specimen.

In general, the purity of the sample is determined by comparing the sample solution with a standard solution, which is prepared by diluting the sample solution to a concentration corresponding to the specified limit amount of the impurity, or by the peak area percentage method.

The peak area percentage method is a method to calculate the proportion of the components from the ratio of the peak area of each component to the sum of the peak areas of every peak recorded in the chromatogram. In order to obtain accurate results in evaluating the proportion of the components, it is necessary to correct the area of each component based on the relative sensitivity to the principal component.

### **7. Loss on Drying Test**

Loss on Drying Test is a method to measure the loss in mass of the sample, when dried under the conditions specified in the monograph. This method is applied to determine the amount of water, all or a part of water of crystallization, or volatile matter in the sample, which is removed during the drying.

The description, for example, not more than 1.0% (1 g, 105°C, 4 hours) in the monograph, indicates that the

loss in mass is not more than 10 mg per 1 g of the substance in the test in which about 1 g of the substance is accurately weighed and dried at 105°C for 4 hours, and not more than 0.5% (1 g, in vacuum, phosphorus (V) oxide, 4 hours), indicates that the loss in mass is not more than 5 mg per 1 g of the substance in the test in which about 1 g of the substance is accurately weighed, transferred into a desiccator (phosphorus (V) oxide), and dried in vacuum for 4 hours.

#### Procedure

Weigh accurately a weighing bottle that has been dried for 30 minutes according to the method specified in the monograph. Take the sample within the range of  $\pm 10\%$  of the amount, directed in the monograph, transfer into the weighing bottle, and, unless otherwise specified, spread the sample so that the layer is not thicker than 5 mm, then weigh it accurately. Place the loaded bottle in a drying chamber, and dry under the conditions specified in the monograph. When the size of the sample is large, convert it to small particles having a size not larger than 2 mm in diameter by quick crushing, and use the crushed sample for the test. After drying, remove from the drying chamber, and reweigh accurately. When the sample is dried by heating, the temperature is within the range of  $\pm 2^\circ\text{C}$  of that, directed in the monograph, and, after drying the bottle, the sample is allowed to cool in a desiccator (silica gel) before weighing.

If the sample melts at a temperature lower than that specified in the monograph, expose the sample for 1 to 2 hours to a temperature between  $5^\circ\text{C}$  and  $10^\circ\text{C}$  below the melting temperature, dry under the conditions specified in the monograph. Use a desiccant specified in the monograph, and renew frequently.

### 8. Ultraviolet-visible Spectrophotometry (Former name: Spectrophotometry)

Ultraviolet-visible Spectrophotometry is a method to measure the degree of absorption of light between the wavelengths of 200 nm and 800 nm by substances for the tests of their identity and purity and for assay. When an atomic absorption spectrophotometer is used for these purposes, proceed as directed under Atomic Absorption Spectrophotometry.

When monochromatic light passes through a substance in the solution, the ratio of transmitted light intensity  $I$  to incident light intensity  $I_0$  is called transmittance  $t$ ; transmittance expressed in the a percentage is called percent transmission  $T$ , and common logarithm of the reciprocal of transmittance is called absorbance  $A$ .

$$t = \frac{I}{I_0} \quad T = \frac{I}{I_0} \times 100 = 100t \quad A = \log \frac{I_0}{I}$$

The absorbance  $A$  is proportional to the concentration  $c$  of a substance in the solution and the length  $l$  of the layer of the solution through which light passes.

$$A = kcl \quad (k = \text{constant})$$

The absorbance, calculated on the basis that  $l$  is 1 cm and  $c$  is 1 mol/L, is called molar absorption coefficient  $\epsilon$ . The molar absorption coefficient at the wavelength of maximum absorption is expressed as  $\epsilon_{\text{max}}$ .

When a light beam passes through a substance in the solution, the absorbance by the sample differs depending on the wavelength of the light. So, an absorption spectrum is obtained by determining the absorbances of a light beam at various wavelengths and by graphically plotting the relation between absorbance and wavelength.

From the absorption spectrum, it is possible to determine the wavelength of maximum absorption  $\lambda_{\max}$  and that of minimum absorption  $\lambda_{\min}$ . The absorption spectrum of a substance in the solution is characteristic, depending on its chemical structure. Therefore, it is possible to identify a substance by comparing the spectrum of a sample within the specified wavelength range with the Reference Spectrum or the spectrum of Reference Standard, by determining the wavelengths of maximum absorption, or by measuring the ratio of absorbances at two specified wavelengths. For the purpose of assay, the absorbance by a sample solution with a certain concentration is measured at the wavelength of the maximum absorption  $\lambda_{\max}$  and compared it with the absorbance of a standard solution with a certain concentration.

### **Apparatus and adjustment**

A spectrophotometer or a photoelectric photometer is used for the measurement of absorbance.

After adjusting the spectrophotometer or photoelectric photometer based on the operation manual of the apparatus, it should be confirmed that the wavelength and the transmission rate meet the specifications of the tests described below.

The calibration of wavelength should be carried out as follows. Using an optical filter for wavelength calibration, measure the transmission rate in the vicinity of the standard wavelength value shown in the test results form, under the test conditions given in the test results form attached to each of the filters. When performing a test to determine the wavelength which shows minimal transmission rate, the difference between the measured wavelength and the standard wavelength value should be within  $\pm 0.5$  nm. When the measurement is repeated three times, each value obtained should be within the mean  $\pm 0.2$  nm. It is also possible to carry out the test using a low-pressure mercury lamp at bright line wavelengths of 253.65 nm, 365.02 nm, 435.84 nm and 546.07 nm, or a deuterium discharge lamp at bright line wavelengths of 486.00 nm and 656.10 nm. In the case of these tests, the difference between the measured wavelength and the wavelength of the bright line should be within  $\pm 0.3$  nm. When the measurement is repeated three times, each value obtained should be within the mean  $\pm 0.2$  nm.

The calibration of transmission rate or absorbance should be carried out as follows. Using an optical filter for transmission rate calibration, determine the transmission rate at the standard wavelength value under the test conditions given in the test results form attached to each of the filters. The difference between the measured transmission rate and the standard transmission rate value should be within the range of from 1% larger of the upper limit to 1% smaller of the lower limit for the relative accuracy shown in the test results form. When the measurement is repeated three times, each absorbance obtained (or calculated from the transmission rate) should be within the mean  $\pm 0.002$  when the absorbance is not more than 0.500, and within the mean  $\pm 0.004$  when the absorbance is more than 0.500. In addition, it will be desirable to confirm the linearity of transmission rate at the same wavelength using several optical filters for calibration of transmission rate with different transmission rates.

### **Procedure**

After adjusting the apparatus as directed in the Apparatus and adjustment, select and set the light source, detector, mode of measurement, measuring wavelength or wavelength range, spectrum width, and scanning speed. Subsequently, allow the apparatus to stand for a certain time to confirm its stability. Then, usually adjust

the apparatus so that the transmittance is 0% at measuring wavelength or over measuring wavelength range after shutting the sample side of light path. Then open the shutter and adjust the transmittance to 100% (the absorbance is zero).

Adjusting the transmittance to 100% is usually done by putting cells containing the control solution in both light paths.

For the control solution, unless otherwise specified, blank solvent is used.

Then perform the measurement with the cell containing the sample solution and read the absorbance at measuring wavelength, or measure the spectrum over measuring wavelength range.

Unless otherwise specified, a cell with a path length of 1 cm, made of quartz for ultraviolet range and of quartz or glass for visible range, is used. Special consideration is needed with the absorption of solvents in the ultraviolet range; use a solvent which does not disturb accurate measurement.

### Specific absorbance

The absorbance, calculated on the basis that  $l$  is 1 cm and  $c$  (concentration of a material) is 1 w/v%, is called specific absorbance, and is expressed as  $E_{1cm}^{1\%}$ .

$$E_{1cm}^{1\%} = \frac{A}{c \times l}$$

$l$ : Length of the layer of the solution (cm)

$A$ : Absorbance value

$c$ : Concentration of the sample in the solution (w/v%)

The description of, for example,  $E_{1cm}^{1\%}$  (241 nm): 500 – 530 (after drying, 2 mg, methanol, 200 mL) in the monograph, indicates that observed  $E_{1cm}^{1\%}$  value is between 500 and 530, when the test is performed in the following manner. The sample is dried under the conditions specified in the Test for Loss on Drying, and about 2 mg of the sample is weighed accurately with a microbalance, and dissolved in methanol to make exactly 200 mL, then the absorbance of the solution is measured as directed in the Procedure at a wavelength of 241 nm using a cell with a path length of 1 cm.

### Identification using absorption wavelength and limit test for contaminants

When maximum absorption wavelengths of the spectrum obtained from the sample solution match the wavelengths specified in the monograph, the identity of the substance may be confirmed. In this case, the range of the wavelength to be compared is the range shown on the Reference Spectrum.

The limit of contaminant in the sample can be confirmed by comparing the limit value specified in the monograph and the absorbance of the sample measured at the wavelength specific to impurities contaminated in the sample.

## 9. Residue on Ignition Test

Residue on Ignition Test is a method to measure the amount of residual substance not volatilized from a sample when the sample is ignited according to the procedure described below. This test is usually used for determining the content of inorganic impurities in an organic substance. In some cases, it is used for determining the content of inorganic substance contained as a component in an organic substance or the content of impurities contained in a volatile inorganic substance.

### Sampling methods

Ignite a suitable crucible (for example, silica, platinum, quartz or porcelain) at  $600\pm 50^{\circ}\text{C}$  for 30 minutes, cool the crucible in a desiccator (silica gel or suitable desiccant) and weigh it accurately.

Unless otherwise specified, weigh accurately 1 g of the sample, and perform the following procedure. When it is directed to perform the test "after drying the sample", weigh a sample dried under the conditions specified in the test for Loss on drying.

### Procedure

#### Method 1

Moisten the sample with a small amount (usually 1 mL) of sulfuric acid, then heat gently at a temperature as low as practicable until the sample is thoroughly charred. After cooling, moisten the residue with a small amount (usually 1 mL) of sulfuric acid, heat gently until white fumes are no longer evolved, and ignite at  $600\pm 50^{\circ}\text{C}$  until the residue is completely incinerated. Ensure that flames are not produced at any time during the procedure. Cool the crucible in a desiccator (silica gel or suitable desiccant), weigh accurately and calculate the percentage of residue.

Unless otherwise specified, if the amount of the residue so obtained exceeds the limit specified in the monograph, repeat the moistening with sulfuric acid, heating and ignition as before, using a 30-minute ignition period, until two consecutive weighings of the residue do not differ by more than 0.5 mg or until the percentage of residue complies with the limit in the monograph.

#### Method 2

Heat gradually the sample, and almost incinerate or volatilize at as low temperature as possible. Moisten it with sulfuric acid, incinerate completely, and ignite to constant mass. Cool in a desiccator (silica gel or suitable desiccant), and weigh the residue accurately.

#### Method 3

Heat the sample gently at first, and ignite gradually ( $800\text{--}1200^{\circ}\text{C}$ ) until the residue is completely incinerated. Cool in a desiccator (silica gel or suitable desiccant), and weigh the residue accurately. If any carbonized substance remains, extract with hot water, filter through a sheet of filter paper for quantitative analysis (5C), and ignite the residue with the filter paper. Add the filtrate to it, evaporate to dryness, and ignite carefully until the carbonized substance does not remain. Cool in a desiccator (silica gel or suitable desiccant), and weigh the residue accurately. If any carbonized substance still remains under this method, add 15 mL of ethanol, crush the carbonized substance with a glass rod, burn the ethanol, ignite carefully and weigh accurately in the same manner.



## 10. Saponification Value Determination

Saponification Value Determination is a method to determine the amount of esters and free acids in the samples. The saponification value is the number of milligrams of potassium hydroxide (KOH: 56.11) required to saponify the esters and to neutralize the free acids in 1 g of the sample.

### Procedure

Unless otherwise specified, weigh accurately 1 g of the sample, transfer to a 200-mL flask, and add exactly 25 mL of 0.5 mol/L potassium hydroxide-ethanol VS. Attach a short reflux condenser or an air condenser 750 mm in length and 6 mm in diameter to the neck of the flask, and heat gently on a water bath for 1 hour with occasional shaking. Cool the solution and titrate the excess potassium hydroxide with 0.5 mol/L hydrochloric acid VS (indicator: phenolphthalein TS). Perform a blank determination in the same manner.

$$\text{Saponification value} = \frac{(a-b) \times 28.053}{c}$$

- a: Volume (mL) of 0.5 mol/L hydrochloric acid VS consumed in the blank determination
- b: Volume (mL) of 0.5 mol/L hydrochloric acid VS consumed for titration of the sample
- c: Amount (g) of sample

## 11. Atomic Absorption Spectrophotometry

Atomic Absorption Spectrophotometry is a method to determine the amount or the concentration of an element in a sample specimen being examined, by utilizing the phenomenon that atoms being in the ground state absorb the light of specific wavelength, characteristic of the respective atom, when the light passes through an atomic vapor layer of the element to be determined.

### Apparatus

Usually, the apparatus consists of a light source, a sample atomizer, a spectroscope, a photometer and a recording system. Some are equipped with a background compensation system. As a light source, usually a hollow cathode lamp specified for each element is used and sometimes a discharge lamp is also used. There are three types of sample atomizer: the flame type, the electrothermal type, and the cold-vapor type. The first one is composed of a burner and a gas-flow regulator, the second one is composed of an electric furnace and a power source, and the third one is composed of a mercury generator and an absorption cell. The third one is further classified into two subtypes, which differ in the atomizing method for mercury containing-compounds: one utilizes chemical reduction-vaporization and the other utilizes a thermal reduction-vaporization method. For the selection of an appropriate analytical wavelength in a spectroscope, a grating for light diffraction or an interference filter can be used. A recording system is composed of a display and a recording device. A background compensation system is employed for the correction of atmospheric effects on the measuring

system. Several principles can be utilized for background compensation, using continuous spectrum sources, the Zeeman splitted spectrum, the nonresonance spectrum, or self-inversion phenomena. Other special options such as a hydride generator and a heating cell, can also be used for analyzing such as selenium. As a hydride generator, a batch method and/or a continuous flow method can be applied. While as a heating cell, there are two kinds of cell: one for heating by flame and the other for heating by electric furnace.

### **Procedure**

Unless otherwise specified, proceed by any of the following methods.

#### **(1) Flame type**

Fit the specific light source to the lamp housing and switch on the instrument. After lighting the lamp and selecting the analytical wavelength specified in the monograph, set an appropriate electric current and a slit-width. Next, a mixture of a combustible gas and a supporting gas is ignited and the gas flow rate and/or pressure should be adjusted to optimum conditions. The zero adjustment of the detecting system must be done through nebulizing the blank solvent into the flame. After setting up the measuring system, the sample solution prepared by the specified procedure is introduced into the flame and the light absorption at the characteristic wavelength of the element to be determined is measured.

#### **(2) Electrothermal type**

Fit the specific light source to the lamp housing and switch on the instrument. After lighting the lamp and selecting the analytical wavelength specified in the monograph, set an appropriate electric current and a slit-width. Further, set an electric furnace to the appropriate temperature, electric current, and heating program, as directed separately in the monograph. When a suitable amount of sample is injected into the heated furnace with an appropriate stream of inert gas, the sample is dried and ashed, simultaneously with atomization of the metallic compound included in the specimen. The atomic absorption specified is observed and the intensity of absorption is measured. Details of the sample preparation method are provided separately in the monograph.

#### **(3) Cold vapor type**

Fit the mercury lamp to the lamp housing and switch on the instrument. After lighting the lamp and selecting the analytical wavelength specified in the monograph, set an appropriate electric current and a slit-width. In the chemical atomization-vaporization method, a mercury containing compound in the sample solution, prepared by the specified procedure, is chemically reduced to metallic mercury by adding a proper reducing reagent to the closed vessel and the generated mercury is vaporized and introduced into the absorption cell with a flow of inert gas. In the thermal atomization-vaporization method, the sample specimen on a quartz dish is heated electrically and the generated atomic mercury is vaporized and introduced into the absorption cell with a flow of inert gas. Thus, in both methods, the generated atomic mercury is carried into the absorption cell as cold vapor and the intensity of the characteristic atomic absorption of mercury is measured.

## **12. Acid Value Determination**

Acid Value Determination is a method to determine the number of milligrams of potassium hydroxide (KOH: 56.11) required to neutralize the free acids in 1 g of sample.

## Procedure

### Method 1

Unless otherwise specified, weigh accurately the amount of sample shown in the Table according to the expected acid value of the sample as well as the amount of solvent in the sample solution and place it in a glass-stoppered 250-mL flask. Add 100 mL (or 50 mL) of ethanol (95) or 100 mL (or 50 mL) of a mixture of diethyl ether and ethanol (95)(1:1 or 2:1) as the solvent, and dissolve the sample by warming if necessary. Then, add a few drops of phenolphthalein TS, and titrate with 0.1 mol/L potassium hydroxide-ethanol VS until the solution develops a light red color which persists for 30 seconds. Perform a blank determination in the same manner, and make any necessary correction.

$$\text{Acid value} = \frac{a \times 5.611}{b}$$

- a: Volume (mL) of 0.1 mol/L potassium hydroxide-ethanol VS consumed  
b: Amount (g) of sample

### Method 2

Unless otherwise specified, weigh accurately the amount of sample shown in the Table, according to the expected acid value of the sample as well as the amount of solvent in the sample solution and place it in a glass-stoppered 250-mL flask. Add 50 mL of ethanol (95) or 50 mL of a mixture of diethyl ether and ethanol (95)(1:1 or 1:2) as the solvent, and dissolve the sample by warming if necessary. Then, add a few drops of phenolphthalein TS, and titrate with 0.1 mol/L potassium hydroxide VS until the solution develops a light red color which persists for 30 seconds. Perform a blank determination in the same manner, and make any necessary correction.

$$\text{Acid value} = \frac{a \times 5.611}{b}$$

- a: Volume (mL) of 0.1 mol/L potassium hydroxide VS consumed  
b: Amount (g) of sample

Table: Amount of sample

The amount of solvent: 100 mL		The amount of solvent: 50 mL	
Acid value	Amount (g) of sample	Acid value	Amount (g) of sample
less than 5	20	less than 5	10
not less than 5 and less than 15	10	not less than 5 and less than 15	5
not less than 15 and less than 30	5	not less than 15 and less than 50	3
not less than 30 and less than 100	2.5	not less than 50 and less than 120	1
not less than 100	1.0	not less than 120	0.5

### 13. Heavy Metals Limit Test

Heavy Metals Limit Test is a limit test of the quantity of heavy metals contained as impurities in a sample. The heavy metals are the metallic inclusions that are darkened with sodium sulfide TS in acidic solution, as their quantity is expressed in terms of the quantity of lead (Pb).

In the monograph, the permissible limit for heavy metals (as Pb) is described in terms of ppm.

#### Preparation of sample solutions and control solutions

Unless otherwise specified, sample solutions and control solutions are prepared as directed in the following.

#### Method 1

Place 1.0 g of the sample in a Nessler tube. Dissolve in water to make 40 mL. Add 2 mL of dilute acetic acid and water to make 50 mL, and designate it as the sample solution.

The control solution is prepared by placing the volume of Standard Lead Solution directed in the following Table (according to the limits specified in the monograph), in a Nessler tube and adding 2 mL of dilute acetic acid and water to make 50 mL.

#### Method 2

Place 1.0 g of the sample in a quartz or porcelain crucible, cover loosely with a lid, and carbonize by gentle ignition. After cooling, add 2 mL of nitric acid and 5 drops of sulfuric acid, heat gradually until the white fumes are no longer evolved, and incinerate by ignition between 500°C and 600°C. Cool, add 2 mL of hydrochloric acid, evaporate to dryness on a water bath, moisten the residue with 3 drops of hydrochloric acid, add 10 mL of hot water, and warm for 2 minutes. Add 1 drop of phenolphthalein TS, add ammonia TS dropwise until the solution develops a pale red color, add 2 mL of dilute acetic acid, filter if necessary, wash with 10 mL of water, transfer the filtrate and washings to a Nessler tube, and add water to make 50 mL. Designate it as the sample solution.

The control solution is prepared as follows: Evaporate a mixture of 2 mL of nitric acid, 5 drops of sulfuric acid, and 2 mL of hydrochloric acid on a water bath, further evaporate to dryness on a sand bath, and moisten the residue with 3 drops of hydrochloric acid. Hereinafter, proceed as directed in the sample solution, then add the volume of Standard Lead Solution directed in the following Table (according to the limits specified in the monograph) and water to make 50 mL.

#### Method 3

Place 1.0 g of the sample in a quartz or porcelain crucible, heat moderately at first and then incinerate by ignition between 450°C and 550°C. After cooling, add 2 mL of hydrochloric acid, evaporate to dryness on a water bath, add 2 mL of dilute acetic acid to the residue, filter if necessary, wash with 10 mL of water, transfer the filtrate and washings into a Nessler tube, add water to make 50 mL, and use this solution as the sample solution.

The control solution is prepared by placing the volume of Standard Lead Solution directed in the following Table (according to the limits specified in the monograph), in a Nessler tube and adding 2 mL of dilute acetic acid and water to make 50 mL.

#### Method 4

Place the sample solution prepared by the method directed in the monograph in a Nessler tube. Separately

place the volume of Standard Lead Solution directed in the monograph in a Nessler tube, add the solution treated in the same manner as the sample solution except for the sample, add further 2 mL of dilute hydrochloric acid and water to make 50 mL, and use this solution as the control solution.

**Procedure**

Add 1 drop of sodium sulfide TS to each of the sample solution and the control solution, mix thoroughly, and allow to stand for 5 minutes. Then compare the colors of both solutions by viewing the tubes downward or transversely against a white background. The sample solution has no more color than the control solution.

Table: Volume of Standard Lead Solution to be taken in the heavy metals limit test  
(amount of the sample, 1.0 g)

Limit	Volume of Standard Lead Solution	Limit	Volume of Standard Lead Solution
10 ppm	1 mL	30 ppm	3 mL
20 ppm	2 mL	50 ppm	5 mL

**14. Infrared Spectrophotometry**

Infrared Spectrophotometry is a method of measurement of the extent, at various wave numbers, of absorption of infrared radiation when it passes through a layer of a substance. In the graphic representation of infrared spectra, the plot usually shows units of wave numbers as the abscissa and units of transmittance or absorbance as the ordinate. Wave number and transmittance or absorbance at each absorption maximum may be read graphically on an absorption spectrum and/or obtained by a data-processor. Since the wave number and the respective intensity of an absorption maximum depend on the chemical structure of a substance, this measurement can be used to identify or determine a substance.

**Apparatus and adjustment**

Several models of dispersive infrared spectrophotometers or Fourier-transform infrared spectrophotometers are available.

The instruments, adjusted according to the instruction manual of each individual instrument, should comply with the following test for resolving power, transmittance reproducibility and wave number reproducibility. When the spectrum of a polystyrene film about 0.04 mm thick is recorded, the depth of the trough from the maximum absorption at about 2850 cm<sup>-1</sup> to the minimum at about 2870 cm<sup>-1</sup> should be not less than 18% transmittance and that from the maximum at about 1583 cm<sup>-1</sup> to the minimum at about 1589 cm<sup>-1</sup> should be not less than 12% transmittance.

The wave number (cm<sup>-1</sup>) scale is usually calibrated by the use of several characteristic absorption wave numbers (cm<sup>-1</sup>) of a polystyrene film shown below. The number in parentheses indicates the permissible range.

3060.0(±1.5)	2849.5(±1.5)	1942.9(±1.5)	1601.2(±1.0)
1583.0(±1.0)	1154.5(±1.0)	1028.3(±1.0)	

When the dispersive infrared spectrophotometer is used, the permissible range of the absorption wave numbers at  $1601.2\text{ cm}^{-1}$  and at  $1028.3\text{ cm}^{-1}$  should be both within  $\pm 2.0\text{ cm}^{-1}$ .

As the repeatability of transmittance and wave number, the difference of transmittance should be within 0.5% when the spectrum of a polystyrene film is measured twice at several wave numbers from  $3000$  to  $1000\text{ cm}^{-1}$ , and the difference of wave number should be within  $5\text{ cm}^{-1}$  at about  $3000\text{ cm}^{-1}$  and within  $1\text{ cm}^{-1}$  at about  $1000\text{ cm}^{-1}$ .

#### **Preparation of samples and measurement**

Unless otherwise specified, when it is directed to perform the test "after drying the sample", use a sample dried under the conditions of "loss on drying" specified in the monograph. Prepare the specimen for the measurement according to one of the following procedures so that the transmittance of most of the absorption bands is in the range of 5% to 80%. Single crystals of sodium chloride, potassium bromide, etc. are available for the optical plate. Generally, the reference cell or material is placed in the reference beam for double-beam instruments, while for single-beam instruments, it is placed in the same optical path in place of the specimen and measured separately under the same operating conditions. The composition and preparation of the reference depend on the sample preparation methods, and sometimes the background absorption of the atmosphere can be utilized.

Unless otherwise specified in the monograph, the spectrum is usually recorded between  $4000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$ . The spectrum should be scanned using the same instrumental conditions as were used to ensure compliance with the requirements for the resolving power and for the precision of wave number scale and of wave numbers.

In specifying absorption wave numbers, wave numbers are rounded off to the nearest  $10\text{ cm}^{-1}$  and add "about" before them if they are not less than  $2000\text{ cm}^{-1}$ .

##### **(1) Potassium bromide disk method**

Powder 1 to 2 mg of a solid sample in an agate mortar, triturate rapidly with 0.10 to 0.20 g of potassium bromide for infrared spectrophotometry with precautions against moisture absorption, and compress the mixture with a press in a suitable die (disk-forming container) to make the sample disk. If necessary to obtain a transparent disk, press the mixture under vacuum of not more than 0.67 kPa in a die with pressure applied to the die of 50 to 100 kN (5000 to 10000 kg) per  $\text{cm}^2$  for 5 to 8 minutes. Prepare a potassium bromide reference disk or a potassium chloride reference disk in the same manner as the sample disk.

##### **(2) Solution method**

Place the sample solution prepared by the method directed in the monograph in a fixed cell for liquid, and usually measure the spectrum against the reference solvent used for preparing the sample solution. The solvent used in this method should not show any interaction or chemical reaction with the specimen to be examined and should not damage the optical plate. The thickness of the fixed cell is usually 0.1 mm or 0.5 mm.

##### **(3) Film method**

Examine the thin film sample just as it is. When the sample is powder, particle, or fiber, etc., unless otherwise specified, prepare the sample film as directed in the following.

- 1) Heat, melt, and compress the sample to prepare the sample film.

- 2) Dissolve the sample in an appropriate solvent, apply to the window plate, and evaporate the solvent to prepare the sample film.

### **Identification**

When several specific absorption wave numbers of the substance being examined are specified in the monograph, a specimen can be identified as being the same substance as the expected substance by confirmation of clear appearance of the absorption bands at all the specified wave numbers.

## **15. Qualitative Tests**

Qualitative Tests are applied to the identification of materials and are done generally with quantities of 2 to 5 mL of the sample solution directed in the monograph.

### **Aluminum salt**

Solutions of aluminum salts, when treated with sodium hydroxide TS, yield a gelatinous, white precipitate which dissolves in an excess of the reagent.

### **Potassium salt**

When the Flame Coloration Test is applied to potassium salts, a pale purple color develops. When it gives a yellow color, a red-purple color can be seen through cobalt glass.

### **Sodium salt**

When the Flame Coloration Test is applied to sodium salts, a yellow color develops.

### **Sulfate**

- (1) Solutions of sulfates yield with barium chloride TS a white precipitate, which does not dissolve upon addition of dilute nitric acid.
- (2) When an equal volume of dilute hydrochloric acid is added, solutions of sulfates yield no white turbidity (discrimination from thiosulfates), and do not evolve the odor of sulfur dioxide (discrimination from sulfites).

## **16. Viscosity Determination**

Viscosity Determination is a method to determine the viscosity of liquid samples using a viscometer.

When a liquid moves in a definite direction, and the liquid velocity has a gradient with respect to the direction rectangular to that of flow, a force of internal friction is generated along both sides of a hypothetical plane parallel to the movement. This flow property of a liquid is expressed in terms of viscosity. The internal friction per unit area on the parallel plane is called slip stress or shear stress, and the velocity gradient with respect to the direction rectangular to that of flow is called slip velocity or shear velocity. A liquid of which the slip velocity is proportional to its slip stress is called a Newtonian liquid. The proportionality constant,  $\eta$ , is a characteristic of a liquid at a certain temperature and is called viscosity. The viscosity is expressed in the unit of Pascal second (Pa·s), and usually milli-Pascal second (mPa·s).

A liquid whose slip velocity is not proportional to its slip stress is called a non-Newtonian liquid. Since the viscosity for a sample of a non-Newtonian liquid changes with its slip velocity, the viscosity measured at a certain slip velocity is called an apparent viscosity. In that case, the value of slip stress divided by the corresponding slip velocity is called an apparent viscosity. Thus, the relationship between apparent viscosity and slip velocity will permit characterization of the flow properties of a given non-Newtonian liquid.

The value of the viscosity,  $\eta$ , divided by the density,  $\rho$ , at the same temperature is defined as a kinematic viscosity,  $\nu$ , which is expressed in the unit of square meter per second ( $\text{m}^2/\text{s}$ ), and usually square millimeter per second ( $\text{mm}^2/\text{s}$ ).

The viscosity of a liquid is determined either by the following Method 1 or Method 2.

#### **Method 1: Viscosity measurement by capillary tube viscometer**

For measuring the viscosity of a Newtonian liquid, a capillary tube viscometer is usually used, in which the downflowing time of a liquid,  $t$  (s), required for a definite volume of the liquid to flow through a capillary tube is measured and the kinematic viscosity,  $\nu$ , is calculated according to the following equation.

$$\nu = Kt$$

Further, the viscosity,  $\eta$ , is calculated from the next equation: where  $\rho$  (g/mL) is the density of the sample measured at the same temperature,  $t$  ( $^{\circ}\text{C}$ ).

$$\eta = \nu\rho = Kt\rho$$

The parameter  $K$  ( $\text{mm}^2/\text{s}^2$ ) represents the viscometer constant and is previously determined by using the Standard Liquids for Calibrating Viscometers with known kinematic viscosity. In the case of a liquid having a similar viscosity to water, water itself can be used as a reference standard liquid for the calibration. The kinematic viscosity of water is  $1.0038 \text{ mm}^2/\text{s}$  at  $20^{\circ}\text{C}$ . In the cases of liquids having a slightly higher viscosity than water, the Standard Liquids for Calibrating Viscometers should be used for the calibration.

The intrinsic viscosity,  $[\eta]$  (dL/g), of a polymer solution is obtained by plotting the relation of viscosity versus concentration and extrapolating the obtained straight line to zero concentration. Intrinsic viscosity shows the degree of molecular expansion of a polymer substance in a given solvent (sample solution) and is also a measure of the average molecular mass of the polymer substance. The downflowing time  $t$  (s) for a polymer solution, whose concentration is  $c$  (g/dL), and  $t_0$  (s) for the solvent used for dissolving the polymer, are measured by using the same viscometer, and then the intrinsic viscosity of a given polymer substance,  $[\eta]$ , is calculated according to the following equation:

$$[\eta] = \lim_{c \rightarrow 0} \frac{(t/t_0) - 1}{c} \quad \text{Or} \quad [\eta] = \lim_{c \rightarrow 0} \frac{\ln(t/t_0)}{c}$$

When the concentration dependency of  $\{(t/t_0) - 1\}/c$  is not large, the value of  $\{(t/t_0) - 1\}/c$  at a concentration directed in the respective monograph can be assumed to be the intrinsic viscosity for a given substance.

The downflowing time of a sample solution is measured with the following apparatus and procedure.

#### **Apparatus**

For measurement of the kinematic viscosity in the range of 1 to  $100,000 \text{ mm}^2/\text{s}$ , the Ubbelohde-type viscometer illustrated in Fig. 1 can be used. The approximate relations between kinematic viscosity range and inside diameter of the capillary tube suitable for the measurement of various liquids with different viscosity,



are given in Table 1. Although a capillary tube viscometer other than the Ubbelohde-type one specified in Table 1 can also be used, a viscometer should be selected in which the downflowing time,  $t$  (s), of a sample solution to be determined would be between 200 s and 1000 s.

### Procedure

Transfer a sample solution gently into a viscometer from the upper end of Tube 1, so that the meniscus of the solution is at a level between the two marked lines of Bulb A when the viscometer is placed vertically. Place the viscometer vertically in a thermostatted bath maintained at the specified temperature within  $\pm 0.1^\circ\text{C}$ , until Bulb C is fully immersed, and let it stand for about 20 minutes to attain the specified temperature. Close tube 3 with a finger and pull the sample solution up to the middle part of Bulb C by gentle suction from the top of Tube 2, taking care not to introduce any bubbles into Tube 2, and stop the suction. Open the end of Tube 3, and immediately close the end of Tube 2. After confirming that the liquid column is cut off at the lowest end of the capillary tube, open the end of Tube 2 to make the sample solution flow down through the capillary tube. Record the time,  $t$  (s), required for the meniscus of the sample solution to fall from the upper to the lower marked line of Bulb B.

Determine the viscometer constant  $K$  previously, using the Standard Liquids for Calibrating Viscometers under the same conditions. The temperature at which the calibration is conducted must be identical with that specified in the monograph.

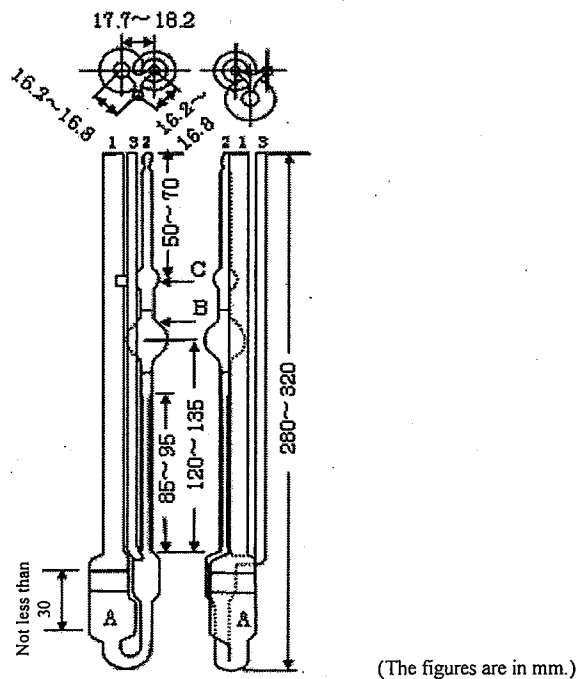


Fig. 1 Capillary tube viscometer

Table 1: Specifications of the Ubbelohde-type viscometer

Viscometer constant ( $K$ )( $\text{mm}^2/\text{s}^2$ )	Inner diameter of capillary tube (mm) Permissible tolerance $\pm 10\%$	Volume of Bulb B (mL) Permissible tolerance $\pm 10\%$	Measuring range of kinematic viscosity ( $\text{mm}^2/\text{s}$ )
0.005	0.46	3.0	1-5
0.01	0.58	4.0	2-10
0.03	0.73	4.0	6-30
0.05	0.88	4.0	10-50
0.1	1.03	4.0	20-100
0.3	1.36	4.0	60-300
0.5	1.55	4.0	100-500
1.0	1.83	4.0	200-1000
3.0	2.43	4.0	600-3000
5.0	2.75	4.0	1000-5000
10.0	3.27	4.0	2000-10000
30.0	4.32	4.0	6000-30000
50.0	5.20	5.0	10000-50000
100.0	6.25	5.0	20000-100000

**Method 2: Viscosity measurement by rotational viscometer**

A rotational viscometer is usually used for measuring the viscosity of Newtonian or non-Newtonian liquids. The measuring principle of a rotational viscometer generally consists in the detection and determination of the force acting on a rotor (torque), when it rotates at a constant angular velocity in a liquid. The extent of torque generated by the rotation can be detected in terms of the torsion of a spring and the liquid viscosity is calculated from the scale-indicated value corresponding to the degree of torsion.

The viscosity of a sample solution is measured with the following apparatus and procedure.

**Apparatus**

Viscosity measurement is performed by using any one of the following three types of rotational viscometers.

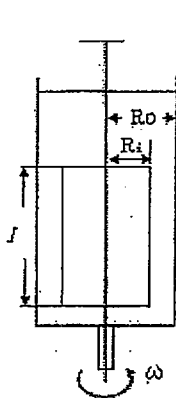


Fig. 2 Coaxial double cylinder-type rotational viscometer

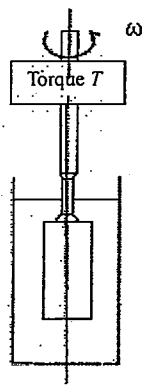


Fig. 3 Single cylinder-type rotational viscometer

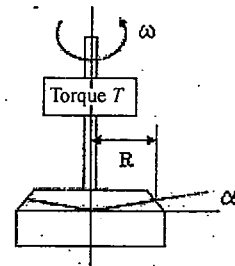


Fig. 4 Cone-flat plate-type rotational viscometer

(1) Coaxial double cylinder-type rotational viscometer (Couette type viscometer)

In the coaxial double cylinder-type rotational viscometer, viscosity is determined by placing a liquid in the gap between the inner and the outer cylinders, which share the same central axis and rotate separately, and the generated torque acting on one cylinder surface when the other cylinder is rotated, and the corresponding angular velocity, are measured.

As shown in Fig. 2, the inner cylinder is hung by a wire whose twist constant is designated as  $k$ . In Fig. 2, half the outer diameter of the inner cylinder and inner diameter of the outer cylinder are designated as  $R_i$  and  $R_o$ , respectively, and the length of the inner cylinder immersed in a liquid is designated as  $l$ . When a liquid is introduced into the gap between the two cylinders, and the outer cylinder is made to rotate at a constant angular velocity,  $\omega$ , the inner cylinder is also forced to rotate due to the viscosity of the liquid. Consequently, torque,  $T$ , is generated by the forced rotation in a viscous liquid, and in the steady state the torque is balanced by the torsion of the wire, as indicated by the degree of rotation  $\theta$ . Then, the relationship can be expressed by  $T = k\theta$  and the viscosity of a liquid,  $\eta$ , is determined from the following equation by measuring the relationship between  $\omega$  and  $\theta$ . Conversely, viscosity measurement can also be performed by rotating the inner cylinder, and the same relationship holds.

$$\eta = \frac{100T}{4\pi l \omega} \left( \frac{1}{R_i^2} - \frac{1}{R_o^2} \right)$$

$\eta$ : Viscosity of a liquid (mPa·s)

$\pi$ : Circumference/diameter ratio

$l$ : Length of the inner cylinder (cm)

$\omega$ : Angular velocity (rad/s)

$T$ : Torque acting on cylinder surface ( $10^{-7}$  N·m)

$R_i$ : 1/2 of outer diameter of the inner cylinder (cm)

$R_o$ : 1/2 of inner diameter of the outer cylinder (cm)

(2) Single cylinder-type rotational viscometer (Brookfield type viscometer)

In the single cylinder-type rotational viscometer, viscosity is determined by measuring the torque acting on the cylinder surface when the cylinder immersed in a liquid is rotated at a given angular velocity. Use an apparatus of the type illustrated in Fig. 3-5. If the apparatus constant  $K_B$  is previously determined experimentally by using the Standard Liquids for Calibrating Viscometers, the viscosity of a liquid,  $\eta$ , can be obtained from the following equation.

$$\eta = K_B \frac{T}{\omega}$$

$\eta$ : Viscosity of a liquid (mPa·s)

$K_B$ : Apparatus constant of viscometer ( $\text{rad}/\text{cm}^3$ )

$\omega$ : Angular velocity (rad/s)

$T$ : Torque acting on cylinder surface ( $10^{-7}$  N·m)

### (3) Cone-flat plate-type rotational viscometer (Coneplate type viscometer)

In the cone-flat plate-type rotational viscometer, viscosity is determined by placing a liquid in the gap between a flat disc and a cone with a large vertical angle sharing the same rotational axis, and the torque and the corresponding angular velocity are measured, when either the disc or the cone is rotated in a viscous liquid. As shown in Fig. 4, a liquid is introduced to fill the gap between a flat disc and a cone forming an angle  $\alpha$  (rad). When either the flat disc or the cone is rotated at a constant angular velocity or a constant torque, the torque acting on the disc or cone surface rotated by the viscous flow and the corresponding angular velocity in the steady state, are measured. The viscosity of the liquid,  $\eta$ , can be calculated from the following equation.

$$\eta = \frac{3\alpha}{2\pi R^3} \cdot \frac{100T}{\omega}$$

$\eta$ : Viscosity of a liquid (mPa·s)

$\pi$ : Circumference/diameter ratio

$R$ : Radius of cone (cm)

$\alpha$ : Angle between flat disc and cone (rad)

$\omega$ : Angular velocity (rad/s)

$T$ : Torque acting on flat disc or cone surface ( $10^{-7}$  N·m)

### Procedure

#### (1) Rotational viscometer

Set up the viscometer so that its rotational axis is perpendicular to the horizontal plane. Prepare the sample solution as directed in the monograph, place a sufficient quantity of a sample solution in the viscometer, and allow the measuring system to stand until a specified temperature is attained, as directed in the monograph.

Where it is desired to measure the viscosity within a precision of 1%, measuring temperature should be controlled within  $\pm 0.1^\circ\text{C}$ . Next, after confirming that the sample solution is at the designated temperature, start operating the rotational viscometer. After the forced rotation induced by the viscous flow has reached a steady state and the indicated value on the scale, which corresponds to the rotational frequency or the torque, has become constant, read the value on the scale. Then, calculate the viscosity  $\eta$  by using the respective equation appropriate to the type of viscometer being used. Determination or confirmation of the apparatus constant should be conducted beforehand by using the Standard Liquids for Calibrating Viscometers, and the validation of the apparatus and operating procedure should also be performed by using those standard liquids.

In the case of a non-Newtonian liquid, repeat the procedure for measuring the apparent viscosity of the liquid with variation of the rotation velocity or torque from one measurement to another. From a series of such viscosity measurements, the relationship between the slip velocity and the slip stress of a non-Newtonian liquid, i.e., the flow characteristics of a non-Newtonian liquid, can be obtained.

Calibration of a rotational viscometer is conducted by using water and the Standard Liquids for Calibrating Viscometers. These standard liquids are used for the determination or confirmation of the apparatus constant of the rotational viscometer. They are also used for periodic recalibration of the viscometer to confirm maintenance of a specified precision.

#### (2) Brookfield type viscometer

Use the rotor in various types and changeable rotation frequency which are suitable for the sample solution.

Prepare Rotor E and Guard F specified in the monograph. Fix the rotation frequency specified in the monograph by Change knob of rotation frequency A. Immerse gently Rotor E into the container filled with the sample solution, so that the surface of the sample solution is on a level with Mark of immersion point D. Switch on, and rotate Rotor E: Indicator B moves from zero on Scale plate C. After Indicator B becomes stable after a lapse of sufficient time, stop the rotor. Measure the value by Indicator B on Scale plate C. Multiply the measuring value by the calculation constant specified in Table 2 by the type of rotor E and its rotation frequency. The resultant value indicates the absolute viscosity (mPa·s) of the sample.

For example, 1500 to 2500 mPa·s (No. 2, 12 rotations, 30 seconds), directed in the monograph, mean that the viscosity of the sample is 1500 to 2500 mPa·s, when No. 2 rotor is rotated for 30 seconds at the frequency of 12 rotations per minute. Otherwise, 30000 to 40000 mPa·s (No. 4, 12 rotations, constant), directed in the monograph, mean that the viscosity of the sample is 30000 to 40000 mPa·s, when No. 4, rotor is rotated at the frequency of 12 rotations per minute until the indicator on the scale plate becomes constant.

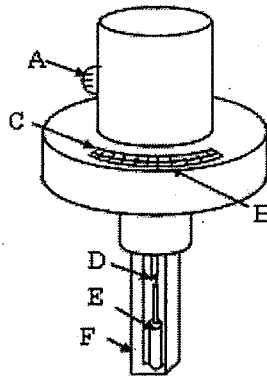


Fig. 5 Rotational viscometer

A: Change knob of rotation frequency, B: Indicator, C: Scale plate, D: Mark of immersion point, E: Rotor, F: Guard

Table 2 Calculation constant

Rotation frequency \ Type of rotor	60	30	12	6
Adaptor	0.1	0.2	0.5	1.0
No.1	1	2	5	10
No.2	5	10	25	50
No.3	20	40	100	200
No.4	100	200	500	1000

## 17. pH Determination

pH is defined as the reciprocal of the common logarithm of hydrogen ion activity, which is the product of hydrogen ion concentration and the activity coefficient. Conventionally, it is used as a scale of hydrogen ion concentration of a sample solution.

pH of a sample solution is expressed by the following equation in relation to the pH of a standard solution ( $pH_s$ ), and can be measured by a pH meter using a glass electrode.

$$pH = pH_s + \frac{E - E_s}{2.3026RT/F}$$

$pH_s$ : pH value of a pH standard solution

$E$ : Electromotive force (volt) induced on the following galvanic cell composed of a glass electrode and suitable reference electrode in a sample solution.

Glass electrode | Sample solution | Reference electrode

$E_s$ : Electromotive force (volt) induced on the following galvanic cell composed of a glass electrode and suitable reference electrode in a pH standard solution.

Glass electrode | pH standard solution | Reference electrode

$R$ : Gas constant

$T$ : Absolute temperature

$F$ : Faraday's constant

The value of  $2.3026 RT/F$  (V) in the above equation means the degree of electromotive force (V) per one pH unit and it is dependent on the temperature as shown in Table 1.

Table 1: Temperature dependency of the electromotive force (V)

Temperature of solution (°C)	2.3026 $RT/F$ (V)	Temperature of solution (°C)	2.3026 $RT/F$ (V)
5	0.05519	35	0.06114
10	0.05618	40	0.06213
15	0.05717	45	0.06313
20	0.05817	50	0.06412
25	0.05916	55	0.06511
30	0.06015	60	0.06610

### pH standard solution

The pH standard solutions are used as a standard of pH, for standardization of a pH meter. To prepare water for preparation of the pH standard solutions, distill purified water, boil the distillate for more than 15 minutes, and cool in a container fitted with a carbon dioxide-absorbing tube (soda lime). Next, prepare individually 6 kinds of pH standard solutions shown in Table 2 by the procedure specified in the following.

Store hermetically the pH standard solutions in hard glass or polyethylene bottles. For storage of alkaline pH standard solutions, it is preferable to use a bottle fitted with a carbon dioxide-absorbing tube. Since the pH

may change gradually during storage over a long period, it is necessary to ascertain whether the expected pH value is held or not by comparison with newly prepared standard, when the solution is used after long storage.

- (1) Oxalate pH Standard Solution: Pulverize potassium trihydrogen dioxalate dihydrate for pH determination, and dry in a desiccator (silica gel). Weigh 12.71 g (0.05 mol) of it accurately, and dissolve in water to make exactly 1000 mL.
- (2) Phthalate pH Standard Solution: Pulverize potassium hydrogen phthalate for pH determination, and dry at 110°C to constant mass. Weigh 10.21 g (0.05 mol) of it accurately, and dissolve in water to make exactly 1000 mL.
- (3) Phosphate pH Standard Solution: Pulverize potassium dihydrogen phosphate for pH determination and disodium hydrogen phosphate for pH determination, and dry at 110°C to constant mass. Weigh 3.40 g (0.025 mol) of potassium dihydrogen phosphate and 3.55 g (0.025 mol) of disodium hydrogen phosphate accurately, and dissolve in water to make exactly 1000 mL.
- (4) Borate pH Standard Solution: Allow sodium tetraborate decahydrate for pH determination to stand in a desiccator (saturated sodium bromide aqueous solution) until it reaches constant mass. Weigh 3.81 g (0.01 mol) of it accurately, and dissolve in water to make exactly 1000 mL.
- (5) Carbonate pH Standard Solution: Dry sodium hydrogen carbonate for pH determination in a desiccator (silica gel) to constant mass, and weigh 2.10 g (0.025 mol) of it accurately. Dry sodium carbonate for pH determination between 300°C and 500°C to constant mass, and weigh 2.65 g (0.025 mol) of it accurately. Dissolve both reagents in water to make exactly 1000 mL.
- (6) Calcium Hydroxide pH Standard Solution: Reduce calcium hydroxide for pH determination to a fine powder, transfer 5 g to a flask, add 1000 mL of water, shake well, and allow the solution to become saturated at a temperature between 23°C and 27°C. Then filter the supernatant at the same temperature and use the clear filtrate (about 0.02 mol/L).

The pH values of these pH standard solutions at various temperatures are shown in the Table 2. pH values at an arbitrary temperature not indicated in Table 2 can be calculated by the interpolation method.

Table 2: Temperature dependency of pH in 6 pH standard solutions

Temperature (°C)	Oxalate pH Standard Solution	Phthalate pH Standard Solution	Phosphate pH Standard Solution	Borate pH Standard Solution	Carbonate pH Standard Solution	Calcium Hydroxide pH Standard Solution
0	1.67	4.01	6.98	9.46	10.32	13.43
5	1.67	4.01	6.95	9.39	10.25	13.21
10	1.67	4.00	6.92	9.33	10.18	13.00
15	1.67	4.00	6.90	9.27	10.12	12.81
20	1.68	4.00	6.88	9.22	10.07	12.63
25	1.68	4.01	6.86	9.18	10.02	12.45
30	1.69	4.01	6.85	9.14	9.97	12.30
35	1.69	4.02	6.84	9.10	9.93	12.14
40	1.70	4.03	6.84	9.07		11.99

50	1.71	4.06	6.83	9.01		11.70
60	1.73	4.10	6.84	8.96		11.45

### Apparatus

A pH meter generally consists of an electrode system of a glass electrode and a reference electrode, an amplifier and an indicating unit for controlling the apparatus and for displaying the measured value of electromotive force. The indicating unit is usually fitted with dials for zero and span (sensitivity) adjustment. Sometimes a temperature compensation dial is included.

The reproducibility of a pH meter should be within  $\pm 0.05$  pH unit, when measurements for an arbitrary pH standard solution are repeated five times, following the procedure described below. After each measurement it is necessary to wash the detecting unit well with water.

### Procedure

Immerse the glass electrode previously in water for more than several hours. Start the measurement after confirming stable running of the apparatus. Rinse well the detecting unit with water, and remove the remaining water gently with a piece of filter paper.

To standardize the pH meter, two pH standard solutions are usually used as follows. Immerse the detection unit in the phosphate pH standard solution and adjust the indicated pH to the pH value shown in the Table by using a zero-adjusting dial. Next, immerse the detection system in the second pH standard solution, which should be selected so that the expected pH of the sample solution to be determined is between the pH values of the two pH standard solutions, and measure the pH under the same conditions as used for the first pH standard solution. Adjust the indicated pH to the defined pH value using the span adjustment dial, when the observed pH is not identical with that tabulated. Repeat the above standardization procedure until both pH standard solutions give observed pH values within  $\pm 0.05$  pH unit of the tabulated value without further adjustments. When a pH meter is fitted with a temperature compensation dial, the standardization procedure is done after the setting of the temperature to that of the pH standard solution to be measured.

In the case of using an apparatus having an auto-calibration function, it is necessary to confirm periodically that the pH values of two pH standard solutions are identical with the tabulated values within  $\pm 0.05$  pH unit. After finishing the standardization procedure described above, rinse well the electrodes with water, remove the attached water using a filter paper, immerse the electrode system in the sample solution, and read the indicated pH value after confirming the value is stable. If necessary, a sample solution can be agitated gently.

In the pH determination, the temperature of a sample solution must be controlled to be the same as that of the pH standard solutions with which the pH meter was standardized (within  $2^{\circ}\text{C}$ ). When a sample solution is alkaline, the measurement should be done in a vessel with a cover and if necessary, in a stream of inert gas such as nitrogen. Furthermore for a strongly alkaline solution above pH 11 containing alkali metal ions, an alkali error may be induced in the pH measurement. Thus, in such a case, an electrode with less alkali error should be used and an appropriate correction should be applied to the measured value.

Note: Construction and treatment in detail are different for different pH meters.



## 18. Determination of Specific Gravity and Density

The density  $\rho$  (g/mL or g/cm<sup>3</sup>) means the mass per unit volume, and the relative density means the ratio of the mass of a sample specimen to that of an equal volume of a standard substance. The relative density is also called the specific gravity.

The specific gravity  $d'_i$  means the ratio of the mass of the sample specimen at  $t^\circ\text{C}$  to that of an equal volume of water (H<sub>2</sub>O) at  $t^\circ\text{C}$ . Unless otherwise specified, the specific gravity is the value of  $d'^{20}$ .

### Method 1: Measurement using a pycnometer

#### (1) Liquid samples

A pycnometer is a glass vessel with a capacity of usually 10 mL to 100 mL, having a ground-glass stopper fitted with a thermometer, and a side inlet-tube with a marked line and a ground-glass cap. Weigh a pycnometer, previously cleaned and dried, to determine its mass  $W$ . Remove the stopper and the cap. Fill the pycnometer with the sample solution, keeping them at a slightly lower temperature by 1°C to 3°C than the specified temperature  $t^\circ\text{C}$ , and stopper them, taking care not to leave bubbles. Raise the temperature gradually, and when the thermometer shows the specified temperature, remove the portion of the sample solution above the marked line through the side tube, cap the side tube, and wipe the outside surface thoroughly. Measure the mass  $W_1$  of the pycnometer filled with the sample solution. Perform the same procedure, using the same pycnometer containing water, and note the mass  $W_w$  at the specified temperature  $t^\circ\text{C}$ . The specific gravity  $d'_i$  can be calculated by use of the following equation.

$$d'_i = \frac{W_1 - W}{W_w - W}$$

Further, when measurements for a sample solution and water are performed at the same temperature ( $t^\circ\text{C} = t^\circ\text{C}$ ), the density of the sample solution at the temperature  $t^\circ\text{C}$  ( $\rho'_T$ ) can be calculated from the measured specific gravity  $d'_i$  and the density of water at the temperature  $t^\circ\text{C}$  ( $\rho'_W$ ) indicated in Table 1 by using the following equation.

$$\rho'_T = \rho'_W d'_i$$

Table 1 Density of water ( $\rho'_W$ )

Temperature °C	Density g/mL	Temperature °C	Density g/mL	Temperature °C	Density g/mL	Temperature °C	Density g/mL
0	0.99984	10	0.99970	20	0.99820	30	0.99565
1	0.99990	11	0.99961	21	0.99799	31	0.99534
2	0.99994	12	0.99950	22	0.99777	32	0.99503
3	0.99996	13	0.99938	23	0.99754	33	0.99470
4	0.99997	14	0.99924	24	0.99730	34	0.99437
5	0.99996	15	0.99910	25	0.99704	35	0.99403
6	0.99994	16	0.99894	26	0.99678	36	0.99368
7	0.99990	17	0.99877	27	0.99651	37	0.99333
8	0.99985	18	0.99860	28	0.99623	38	0.99297

9	0.99978	19	0.99841	29	0.99594	39	0.99259
10	0.99970	20	0.99820	30	0.99565	40	0.99222

## (2) Solid samples

A pycnometer which is suitable for solid samples is used. Use the sample pulverized appropriately. If the sample is in the form of powders, granules, pellets or flakes of measurable size, use the sample as it is. Weigh a pycnometer, previously cleaned and dried, to determine its mass  $W$  down to the degree of 1.0 mg. Place an adequate amount of sample in the pycnometer and measure its mass  $W_1$ . Add the immersion liquid, keeping the temperature of the liquid 1 to 3°C lower than the specified temperature  $t^{\circ}\text{C}$ , to immerse the sample. Place the pycnometer in a desiccator and hold it with vacuum to remove air completely. Return the pressure to ordinal, fill the pycnometer with the immersion liquid, place the pycnometer in a water bath and keep it at the specified temperature  $t^{\circ}\text{C}$ . Next, exactly fill the pycnometer to its capacity with the immersion liquid, wipe out the attached liquid thoroughly and measure its mass  $W_2$ . Empty the pycnometer, clean, wipe it. Then, fill the pycnometer with boiled and cooled distilled water, deaerate it in the same manner as described above, and measure the mass  $W_w$  at the specified temperature  $t^{\circ}\text{C}$ . When water is used as the immersion liquid, the specific gravity  $d'_i$  ( $t' = t$ ) can be calculated by the following equation.

$$d'_i = \frac{W_1 - W}{(W_w - W) - (W_2 - W_1)}$$

When the immersion liquid other than water is used, follow the same procedure using the given immersion liquid, measure the mass  $W_{IL}$  and calculate the density ( $\rho'_{IL}$ ) of that immersion liquid by using the following equation.

$$\rho'_{IL} = \frac{W_{IL} - W}{W_w - W} \times \rho'_w$$

$\rho'_w$ : Density ( $\text{g/cm}^3$ ) of water at the specified temperature  $t$  (see Table 1)

The density of the sample ( $\rho'_T$ ) can be calculated by the equation.

$$\rho'_T = \frac{(W_1 - W) \times \rho'_{IL}}{(W_{IL} - W) - (W_2 - W_1)}$$

When  $t'$  is not equal to  $t$ , the specific gravity  $d'_i$  of the sample can be calculated by using the density of water at  $t$  ( $\rho'_w$ , Table 1) by the following equation.

$$d'_i = \frac{\rho'_T}{\rho'_w}$$

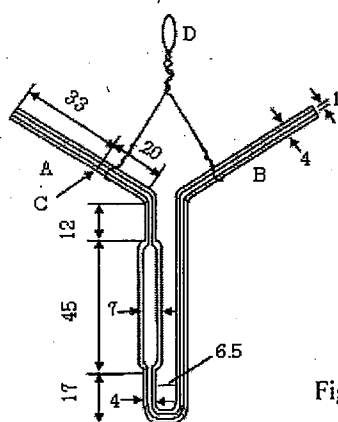
### Immersion liquid

The immersion liquid is the liquid with known density which does not dissolve, swell or react with the sample and whose specific gravity is lower than that of the sample. Usually, new distilled water, purified mineral oil, etc. are used. No more than 0.1% of an appropriate moistening agent may be added to the immersion liquid to expel any entrapped air bubbles.

### Method 2: Measurement using a Sprengel-Ostwald pycnometer

A Sprengel-Ostwald pycnometer is a glass vessel with a capacity of usually 1 mL to 10 mL. As shown in Fig. 1, both ends are thick-walled fine tubes (inside diameter: 1-1.5 mm, outside diameter: 3-4 mm), one of which, tube A, has a line marked C on it. Determine the mass of a pycnometer,  $W$ , previously cleaned and dried, by hanging it on the arm of a chemical balance with a platinum or aluminum wire D. Immerse the fine tube B in the sample solution, which is at a lower temperature by 3°C to 5°C than the specified temperature  $t^\circ\text{C}$ . Attach rubber tubing or a ground-glass tube to the end of A, and suck up the sample solution until the meniscus is above the marked line C, taking care to prevent bubble formation. Immerse the pycnometer in a water bath kept at the specified temperature  $t^\circ\text{C}$  for about 15 minutes, and then, by attaching a piece of filter paper to the end of B, adjust the level of the sample solution to the marked line C. Take the pycnometer out of the water bath, wipe thoroughly the outside surface and determine the mass  $W_1$ . By use of the same pycnometer, perform the same procedure for the standard solution of water. Weigh the pycnometer containing water at the specified temperature  $t^\circ\text{C}$ , and note the mass  $W_w$ . Calculate the specific gravity  $d'_i$  according to the following equation.

$$d'_i = \frac{W_1 - W}{W_w - W}$$



(The figures are in mm.)

Fig. 1 Measurement using a Sprengel-Ostwald pycnometer

Further, when measurements for a sample solution and water are performed at the same temperature ( $t^\circ\text{C} = t^\circ\text{C}$ ), the density of the sample solution at the temperature  $t^\circ\text{C}$  ( $\rho'_T$ ) can be calculated from the measured specific gravity  $d'_i$  and the density of water at the temperature  $t^\circ\text{C}$  ( $\rho'_w$ ) indicated in Table 1 by using the following equation.

$$\rho'_T = \rho'_w d'_i$$

### Method 3: Measurement using an oscillator-type density meter

Density measurement with an oscillator-type density meter is a method for obtaining the density of liquid or gas by measuring the intrinsic vibration period  $T$  (s) of a glass tube cell filled with sample specimen. When a glass tube containing a sample is vibrated, it undergoes a vibration with an intrinsic vibration period  $T$  in proportion to the mass of the sample specimen. If the volume of the vibrating part of the sample cell is fixed, the relation of the square of intrinsic oscillation period and density of the sample specimen shall be linear. Before measuring a sample density, the respective intrinsic oscillation periods  $T_{S1}$  and  $T_{S2}$  for two reference substances (density:  $\rho_{S1}$ ,  $\rho_{S2}$ ) must be measured at a specified temperature  $t^\circ\text{C}$ , and the cell constant  $K_t$  ( $\text{g}\cdot\text{cm}^{-3}$ )

s<sup>2</sup>) must be determined by using the following equation.

$$K_t = \frac{\rho_{S1}' - \rho_{S2}'}{T_{S1}^2 - T_{S2}^2}$$

Usually, water and dried air are chosen as reference substances. Here the density of water at  $t^\circ\text{C}$ ,  $\rho_{S1}'$ , is taken from the Table 1, and that of dried air  $\rho_{S2}'$  is calculated by using the following equation, where the pressure of dried air is at  $p$  kPa.

$$\rho_{S2}' = 0.0012932 \times \{273.15 / (273.15 + t')\} \times (p / 101.325)$$

Next, introduce a sample specimen into a sample cell having a cell constant  $K_t$ , the intrinsic vibration period,  $T_T$ , for the sample under the same operation conditions as employed for the reference substances. The density of a sample specimen at  $t^\circ\text{C}$ ,  $\rho_T'$ , is calculated by use of the following equation, by introducing the intrinsic oscillation period  $T_{S1}$  and the density of water at a specified temperature  $t^\circ\text{C}$ ,  $\rho_{S1}'$ , into the equation.

$$\rho_T' = \rho_{S1}' + K_t(T_T^2 - T_{S1}^2)$$

Further, the specific gravity of a sample specimen against water at a temperature  $t^\circ\text{C}$ ,  $d_t'$ , can be obtained by using the equation below, by introducing the density of water at a temperature  $t^\circ\text{C}$ ,  $\rho_W'$ , indicated in Table 1.

$$d_t' = \frac{\rho_T'}{\rho_W'}$$

### Apparatus

An oscillator-type density meter is usually composed of a glass tube cell of about 1 mL capacity, the curved end of which is fixed to the vibration plate, an oscillator which applies an initial vibration to the cell, a detector for measuring the intrinsic vibration period, and a temperature controlling system.

A schematic illustration of the apparatus is depicted in Fig. 2.

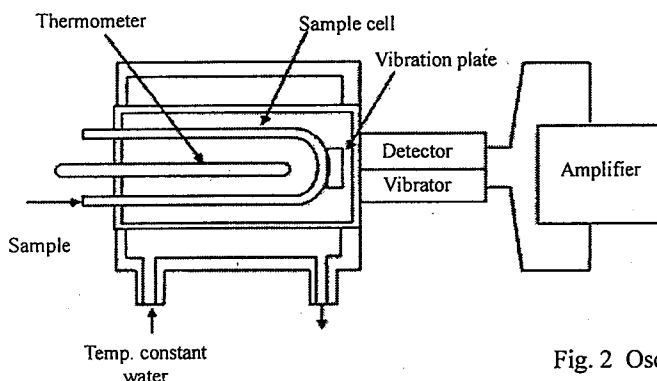


Fig. 2 Oscillator-type density meter

### Procedure

A sample cell, water, and a sample specimen are previously adjusted to a specified temperature  $t^\circ\text{C}$ . Wash the sample cell with water or an appropriate solvent, and dry it thoroughly with a flow of dried air. Stop the flow of dried air, confirm that the temperature is at the specified value, and then measure the intrinsic oscillation period  $T_{S2}$  given by the dried air. Separately, the atmospheric pressure  $p$  (kPa) must be measured at the time and place of the examination. Next, introduce water into the sample cell and measure the intrinsic oscillation period  $T_{S1}$  given by water. Using these values of the intrinsic oscillation period and the atmospheric pressure,

the sample cell constant  $K_T$  can be determined by use of the above-mentioned equation.

Next, introduce a sample specimen into the glass cell, confirm the specified temperature, and measure the intrinsic oscillation period  $T_T$  given by the sample specimen. Using the intrinsic oscillation periods for water and the sample specimen, the density of water  $\rho_{S,T}'$ , and the cell constant  $K_T$ , the density of the sample specimen  $\rho_T'$  can be obtained by use of the above equation. If necessary, the specific gravity of the sample specimen  $d_i'$  against water at a temperature  $t^\circ\text{C}$ , can be calculated by using the density of water  $\rho_W'$  shown in Table 1.

In this measurement, avoid the occurrence of bubble formation in the sample cell, when a sample specimen or water is introduced into the cell.

#### **Method 4: Sink-float method**

This method is used to measure the specific gravity of a chemical fiber sample or a plastic sample such as granule, pellet or flake.

##### **(1) Chemical fiber samples**

Immerse about 0.1 g of the fiber sample in about 20 mL of an appropriate deoiling liquid shown in Table 2 for about 1 hour. After remove oil, air-dry the sample, cut into 0.5 mm to 1.0 mm pieces using a razor etc., and using a vacuum desiccator with the pressure not exceeding 0.5 kPa dry these pieces completely before use. Place about 8 mL of the prepared specific gravity determination liquid in the sedimentation tube and put a small amount of the sample in it. Stopper the sedimentation tube, disperse the sample well, centrifuge to expel any entrapped air bubbles and immerse the tube in a water bath maintained at the specified temperature  $t^\circ\text{C} \pm 0.1^\circ\text{C}$  for about 30 minutes. Observe whether the sample sinks or floats and add an adequate amount of either heavy or light liquid shown in Table 3 according to its condition to adjust the specific gravity of the specific gravity determination liquid so that the sample reaches equilibrium in the liquid. After adjustment, allow the tube to stand in the water bath for 30 minutes and confirm that the sample exists still in equilibrium in the liquid. Then, measure the specific gravity of the liquid in the cylinder as directed in Methods 1 to 3 and designate it as the specific gravity of the sample ( $d_i'$ ).

##### **Specific gravity determination liquid**

Mix adequate amounts of a heavy liquid and a light liquid for fiber sample shown in Table 3 in a measuring cylinder so that the specific gravity of the mixture is within  $\pm 0.02$  of the expected specific gravity of the sample.

Table 2: Liquids used for deoiling chemical fiber samples

Fiber	Deoiling liquid
Polyester	Methanol
Acetate	Diethyl ether
Polypropylene	Ethanol
Other	Mixture of ethanol and benzene (capacity ratio 1:2)

Table 3: Heavy and light liquids

Fiber	Heavy liquid	Light liquid
Polypropylene	Water	Ethanol
Polyester	Perchloroethylene	n-Heptane
Other	Perchloroethylene	Toluene

(2) Plastic samples such as granules, pellets or flakes

Transfer exactly 100 mL of the prepared specific gravity determination liquid into a 250 mL measuring cylinder and immerse the cylinder in a water bath maintained at  $t^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ . Put some of the samples in a cylinder, and sink them to the bottom to avoid formation of bubbles. Allow the cylinder to stand for about 5 minutes and stir several times so that the temperature remains stable at the specified temperature  $t^{\circ}\text{C}$ : Observe whether the sample sinks or floats and add an adequate amount of either heavy or light liquid according to its condition to adjust the specific gravity of the specific gravity determination liquid so that the sample reaches equilibrium in the liquid. After adjustment, allow the cylinder to stand in the water bath for a while and confirm that the sample exists still in equilibrium. Then, measure the specific gravity of the liquid in the cylinder as directed in Methods 1 to 3 and designate it as the specific gravity of the sample ( $d'_t$ ).

#### Specific gravity determination liquid

The heavy and light liquids are freshly distilled liquids having different densities, which are compatible and do not dissolve, swell or react with the sample. Mix adequate amounts of a heavy liquid and a light liquid so that the specific gravity of the mixture is within  $\pm 0.02$  of the expected specific gravity of the sample, and use as the specific gravity determination liquid at the start of the measurement.

#### Method 5: Measurement using density gradient tube

When a solid sample is placed in the liquid, it sinks if its density is greater than that of the liquid and it floats if its density is smaller than that of the liquid, and it remains suspended if its density is equal to that of the liquid. The density gradient tube method works on this principle. This method is applicable for a sample having a volume not exceeding  $0.5 \text{ cm}^3$  and when the density gradient liquid used for this test does not dissolve, swell or react with the sample.

The density gradient tube is a vertically-placed glass cylinder with graduations, and prepared by injecting two liquids having the different densities while continuously changing the mixing ratio. The relation between the graduation of the density gradient tube and the density should be calibrated using a standard float.

#### Apparatus

It is shown in Fig. 3.

- Glass cylinder: Use a glass cylinder 1 m in length and having an inside diameter of 4.5 cm, with a stopper on the top, having 1 mm graduation lines along the length of not less than 85 cm and 10 mm graduation lines around the circumference and the figures displayed at intervals of 1, 2 or 5 cm. If appropriate, glass cylinders of different sizes can be used.
- Glass containers: Use two 1000 mL or about 2000 mL glass containers having the same diameter.
- Siphon: Use a siphon as shown in Fig. 3.

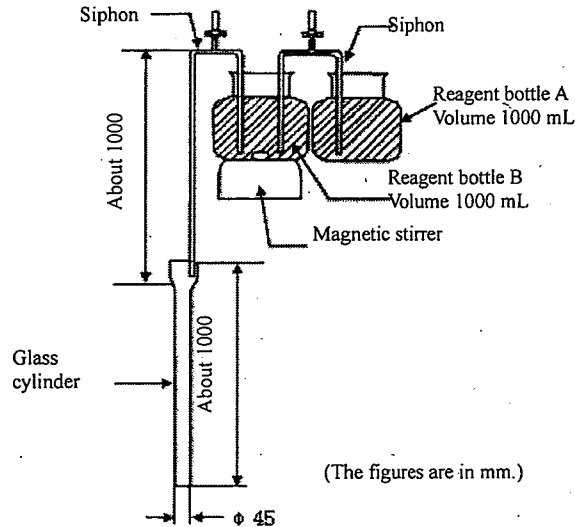


Fig. 3 Density gradient tube

### Standard floats

Use hollow glass balls, which are 2 to 5 mm in diameter, the densities of which are accurately determined to the same digit as specified in the required measurement result.

### Preparation of density gradient tube

Prepare a density gradient tube as follows.

- To determine the densities  $\rho_A$  and  $\rho_B$  ( $\rho_A < \rho_B$ ) of two liquids which consist of the density gradient liquid by using the following equation.

$$\rho_A = \rho_B - \frac{2(\rho_B - \rho) \times V_B}{V}$$

$\rho_A$ : Initial density ( $\text{g/cm}^3$ ) of the liquid in glass container A

$\rho_B$ : Initial density ( $\text{g/cm}^3$ ) of the liquid in glass container B

$\rho$ : Density ( $\text{g/cm}^3$ ) of the liquid in the uppermost part of the density gradient tube

$V_B$ : Initial volume (mL) of the liquid in glass container B

$V$ : Total volume (mL) of the liquid in the density gradient tube

When measurements down to the third decimal place are required, prepare a density gradient tube of which density difference between the tube bottom and tube top does not exceed  $0.2 \text{ g/cm}^3$ .

- Prepare two liquids having the densities specified in a) according to Tables 3, 4, and 5 and determine their densities according to Methods 1 to 3. Sufficiently deaerated liquid is used. When water is used, it is boiled or decompressed before use.
- Place the liquid of a lower density in the glass container A in Fig. 3 and the liquid of a higher density in the glass container B, make the level of both liquid equal, and connect with a siphon filled with the liquid of a lower density.
- While stirring the liquid in the glass container B with a stirrer, inject the liquid in the container into the glass cylinder along the wall of the cylinder at the rate of 20 mL/min or lower using a siphon.
- Perform procedures b) to d) at the specified temperature  $t^\circ\text{C}$ .
- Stopper the glass cylinder, place it slowly in a water bath maintained at the specified temperature  $t^\circ\text{C}$ ,

and allow to stand for not less than 1 hour. When measurements down to the third decimal place are required, allow the density gradient tube to stand in a water bath maintained at  $t^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ .

- g) Wet a standard float with the liquid in the glass container A, place it gently in the cylinder, stopper it, and use this as the density gradient tube. When measurements down to the third decimal place are required, more than one standard floats are appropriate per density difference of 0.01.
- h) After 24 hours, read the height of the gravity center of the standard float in the density gradient tube to 1 mm from graduations of the density gradient tube, and prepare a calibration curve indicating the relation between the density of the standard float and the graduation of the density gradient tube. The accuracy of the calibration curve should be  $\pm 1$  mm.
- i) If the calibration curve is not a smooth curve or markedly curved, repeat the above procedures from a) to h).

#### Density gradient liquid

A density gradient liquid should not dissolve or swell a solid sample. The two liquids which consist of a density gradient liquid should be compatible. Representative examples of density gradient liquids and the applicable density range are shown in Table 4. Reagents for density adjustment used for various mixtures are shown in Table 5.

Table 4 Examples of density gradient liquids

Liquids	Density range ( $\text{g}/\text{cm}^3$ )
Methanol / Benzyl alcohol	0.80-0.92
2-Propanol / Water	0.79-1.00
2-Propanol / Diethylene glycol	0.79-1.11
Ethanol / Carbon tetrachloride	0.79-1.59
Ethanol / Water	0.79-1.00
Toluene / Carbon tetrachloride	0.87-1.59
Water / Sodium bromide	1.00-1.41
Water / Calcium nitrite	1.00-1.60
Zinc chloride / Ethanol / Water	0.80-1.70
Carbon tetrachloride / 1,3-Dibromopropane	1.60-1.99
1,3-Dibromopropane / Ethylene bromide	1.99-2.18
Ethylene bromide / Bromoform	2.18-2.89
Carbon tetrachloride / Bromoform	1.60-2.89
2-Propanol / Methyl glycol acetate	0.79-1.00

Table 5 Examples of reagents for density adjustment

Reagent name	Density ( $\text{g}/\text{cm}^3$ )
n-Octane	0.70
Dimethylformamide	0.94
Ethane tetrachloride	1.59
Ethyl iodide	1.93



**Procedure**

Dry the sample sufficiently, prepare 3 samples from the identical sample, and use these samples as the samples for measurement. The samples should be stored in a desiccator with a desiccant. The length of the largest part of each sample should be not more than one-fourth the inside diameter of the density gradient tube and the volume of each sample should be not more than  $0.5 \text{ cm}^3$  (usually, 2 to 5 mm  $\times$  2 to 5 mm). If the sample is a chemical fiber, deoil the sample as directed in Method 4, air-dry, and tie in a ring having a diameter of 3 mm.

When multiple samples are put in simultaneously and measured using the existing calibration curve, the size of each sample should be adjusted so that the increased level of liquid surface due to charge-in of all samples should not exceed 1 mm.

Wet three samples with the liquid having a lower density and place them gently in the density gradient tube, taking care to avoid formation of air bubbles. If the samples are fiber, allow the samples in the liquid with a low density to stand under reduced pressure of 0.7 kPa for 5 minutes or centrifuge at 2000 to 3000  $\text{min}^{-1}$  for 2 to 3 minutes to expel any entrapped air bubbles.

After the sample reaches equilibrium and exists still, read the level of the gravity center to 1 mm from graduations of the density gradient tube. If the sample contacts with the standard float or the inner wall of the tube, perform the test again. Compare the readings and calibration curve, read the density corresponding to each sample to the same digit number as required accuracy.

Determine the mean density,  $\rho'_r$  of three samples at the specified temperature  $t^\circ\text{C}$ , designate it as the density of the sample and round off to the same decimal place as that of the calibration density of the standard float. If the density gradient per mm of the density gradient tube exceeds the change in one, the last digit of the calibration density of the standard float, round off to one place higher than that of the calibration density of the standard float. Calculate the specific gravity of the sample  $d'_i$  by using the following equation from the density determined above and the density of water  $\rho'_w$  at  $t^\circ\text{C}$  in Table 1, and round off to the same decimal place as that of the density.

$$d'_i = \frac{\rho'_r}{\rho'_w}$$

**19. Arsenic Limit Test**

Arsenic Limit Test is a limit test for arsenic contained in a sample. The limit is expressed in terms of arsenic (III) trioxide ( $\text{As}_2\text{O}_3$ ). In each monograph, the permissible limit for arsenic (as  $\text{As}_2\text{O}_3$ ) is described in terms of ppm in parentheses.

**Apparatus**

Use the apparatus shown in the figure.



## Method 2

Unless otherwise specified, weigh 1.0 g of the sample, and place it in a crucible of platinum, quartz, or porcelain. Add 10 mL of a solution of magnesium nitrate hexahydrate in ethanol (95) (1 in 50), ignite the ethanol, and heat gradually to incinerate. If a carbonized residue still remains, moisten the residue with a little amount of nitric acid, and ignite again to incinerate. After cooling, add 3 mL of hydrochloric acid, heat on a water bath to dissolve the residue, and designate it as the sample solution.

### Test solutions

Absorbing solution for hydrogen arsenide: Dissolve 0.50 g of silver N,N-diethyldithiocarbamate in pyridine to make 100 mL. Preserve this solution in a glass-stoppered bottle protected from light, in a cold place.

Standard Arsenic Stock Solution: Weigh accurately 0.100 g of finely powdered arsenic (III) trioxide dried at 105°C for 4 hours, and add 5 mL of sodium hydroxide solution (1 in 5) to dissolve. Add dilute sulfuric acid to neutralize, add further 10 mL of dilute sulfuric acid, and add freshly boiled and cooled water to make exactly 1000 mL.

Standard Arsenic Solution: Pipet 10 mL of Standard Arsenic Stock Solution, add 10 mL of dilute sulfuric acid, and add freshly boiled and cooled water to make exactly 1000 mL. Each mL of the solution contains 1 µg of arsenic (III) trioxide ( $As_2O_3$ ). Prepare before use and preserve in a glass-stoppered bottle.

### Procedure

Unless otherwise specified, proceed using apparatus shown in Figure.

Carry out the preparation of the standard color at the same time.

Place the sample solution in the generator bottle A, and, if necessary, wash down the solution in the bottle with a small quantity of water. Add 1 drop of methyl orange TS, and after neutralizing with ammonia TS, ammonia solution (28), or dilute hydrochloric acid, add 5 mL of diluted hydrochloric acid (1 in 2) and 5 mL of potassium iodide TS, and allow to stand for 2 to 3 minutes. Add 5 mL of acidic tin (II) chloride TS, and allow to stand for 10 minutes. Then add water to make 40 mL, add 2 g of zinc for arsenic analysis, and immediately connect the rubber stopper H fitted with B and C with the generator bottle A. Transfer 5 mL of the absorbing solution for hydrogen arsenide to the absorber tube D, insert the tip of C to the bottom of the absorber tube D, then, immerse the generator bottle A up to the shoulder in water maintained at 25°C and allow to stand for 1 hour. Disconnect the absorber tube, add pyridine to make 5 mL if necessary, and observe the color of the absorbing solution: the color produced is not more intense than the standard color.

Preparation of standard color: Measure accurately 2 mL of Standard Arsenic Solution in the generator bottle A. Add 5 mL of diluted hydrochloric acid (1 in 2) and 5 mL of potassium iodide TS, and allow to stand for 2 to 3 minutes. Add 5 mL of acidic tin (II) chloride TS, allow to stand at room temperature for 10 minutes, and then proceed as directed above. The color produced corresponds to 2 µg of arsenic (III) trioxide ( $As_2O_3$ ) and is used as the standard.

Note: Apparatus, reagents, and test solutions used in the test should contain little or no arsenic. If necessary, perform a blank determination.